# Fullerene as Photocatalyst: Visible-Light Induced Reaction of Perfluorinated α,ω-Diiodoalkanes with C_{60}

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S *Supporting Information*

ABSTRACT: Solution phase photochemical reaction of fullerene with perfluorinated alkyldiiodides $I-R_F-I$ can be efficiently initiated by visible range irradiation that targets solely the fullerene component. Photoinduced electron transfer from fullerene onto the diiodide component effects dissociative formation of alkyl radicals $R_F I^\bullet$ subsequently consumed by C_{60}

$$C_{60} + IR_FI \xrightarrow[>400\ nm]{h\nu} \overset{\overset{\bar{e}}{\frown}}{C_{60}\cdots IR_FI} \longrightarrow C_{60}^{+\bullet}I^- + {}^\bullet R_FI \xrightarrow{C_{60}} {}^\bullet C_{60}R_FI, \ (C_{60}R_FI)_2, \ XC_{60}R_FI \quad (X = H, I)$$

to give the principal detectable radical intermediate $C_{60}R_FI^\bullet$. Experimentally established second-order kinetics with respect to the fullerene concentration evidence that fullerene plays its two roles of photocatalyst and reactant in a decoupled fashion, which suggests its catalytic ability to be of potential use in more complex photochemical systems. The main final product of the photochemical transformation observed is the singly linked dimer of the intermediates, $I-R_F-C_{60}-C_{60}-R_F-I$. Side reactions of $C_{60}R_FI^\bullet$ with the environment lead to quenching of the unpaired electron density by *ortho-* or *para-* attachment of hydrogen or iodine. The outlined kinetic findings are discussed in detail.
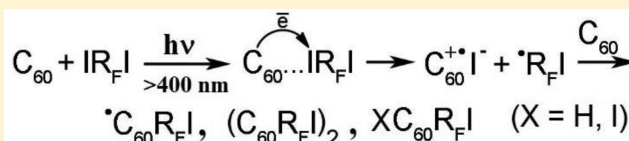
INTRODUCTION

Fullerenes readily enter into radical reactions, usually resulting in a wide variety of addition products, in which different groups like halogens, alkyl, perfluoroalkyl, alkylsilyl, *etc.* are attached to the fullerene cage.[1] The radicals in such reactions can be generated thermally or photochemically. In particular, formation of perfluoroalkyl derivatives of fullerene occurs through reactions with perfluoroalkyl iodides R_FI, trifluoroacetates of metals or fluoroalkylperoxides, which easily form perfluoroalkyl radicals $R_F^\bullet$ upon heating.[2] Photochemical synthesis of perfluoroalkyl fullerene derivatives under UV irradiation of various sources of radicals has also been described. Such synthesis results in the formation of a mixture of poly adducts $C_{60}(R_F)_n$.[3] Currently there are much data in the literature concerning trifluoromethyl[4,5] pentafluoroethyl,[6,7] and heptafluoropropyl[8,9] derivatives of C_{60} and C_{70}. The first reports on the cyclization of perfluoroalkane fragments on fullerenes were recently published.[10,11] The products of cycloalkylation were obtained in reactions with $C_2F_4I_2$[10] and $C_4F_8I_2$.[11] The derivatives $C_{60}(C_4F_8)_n$ (n = 2, 3, 4, and 6) were separated and characterized in these works. Along with the expected motives of addition [4 + 2] and [2 + 2], the motive [4 + 3] with the formation of a seven-member cycle was detected.

The formation of active radical particles at photo excitation has been studied for $C_2F_4I_2$ molecules.[12,13] It was found that the excited molecule detaches the first iodine atom with the formation of $C_2F_4I^\bullet$ radical within 200 fs. The second iodine atom comes off after 25 ps.

It is known[3] that radical particles attack a fullerene molecule according to the reaction $C_{60} + X^\bullet \rightarrow XC_{60}^\bullet$. The resulting fullerene radicals were fixed by ESR spectroscopy.[2,3] Recently, the identification of $C_{60}(R_F)_{2k+1}^\bullet$ free radicals (R_F = CF_3, C_2F_5)

by means of MALDI-ref-TOF MS has been reported.[14] The applied procedure was based on the fact that in the case of fullerene derivatives an odd-numbered $C_{60}(R_F)_n^-$ stable fragment peak has to be accompanied by a metastable one.[15] The absence of the latter indicates that the odd-numbered $C_{60}(R_f)_n^-$ ion corresponds to a free radical.

It has been experimentally determined that the stability of fullerene radical intermediates is generally conditioned by the volume of a substitute.[16] Sabirov and co-workers have studied the radicals $RC_{60}^\bullet$, $ROC_{60}^\bullet$, and $ROOC_{60}^\bullet$ by means of density functional theory.[17] The results indicate that the formation of bis-adducts $C_{60}X_2$ is the most exothermic way of further transforming fullerene radical intermediates. The most thermodynamically favorable products are 1,4- and 1,16-$C_{60}R_2$ in the case of alkyls, 1,4- and 1,2-$C_{60}(OR)_2$ in the case of alkoxiles, and 1,2- and 1,4-$C_{60}(OOR)_2$ in the case of alkylperoxy radicals. Slightly less exothermic is the reaction of formation of 1,4,1′,4′-dimers. Lastly, the reaction with oxygen molecules is the least thermodynamically favorable way of transformation for the $RC_{60}^\bullet$ radicals.

Reasoning from the above-mentioned knowledge one can expect the formation of iodine-containing radicals $C_{60}R_FI^\bullet$ as intermediates of cycloalkylation reactions. In the present work it was presumed study of radical particles in photochemical reaction with the diiodides $C_2F_4I_2$, $C_4F_8I_2$ and with monoiodide CF_3I for comparison. The aim of the investigation was the determination of the spectroscopic properties, conditions of formation and further reactions of iodine-containing radical

particles $C_{60}R_FI^{\bullet}$, as well as the possibility of control over cycloalkylation processes. We applied gentle and a rather easily governed photochemical method of generation of the primary radicals and monitored the progress of the reaction by UV−vis spectrophotometry and ESR spectroscopy. The goal of the present study was also to elucidate the possibility of registering radical fullerene derivatives by means of MALDI mass spectrometry.

EXPERIMENTAL AND THEORETICAL METHODS

Sample Preparation. The samples studied were *n*-hexane, toluene, decalin, *o*-dichlorobenzene, or 1,2,4-trichlorobenzene solutions, containing C_{60} (4×10^{-5} to 1.2×10^{-2} M) and $C_4F_8I_2$ or $C_2F_4I_2$ (0.002−0.82 M). The solutions were placed in a special vessel, shown in Figure 1. Valve 4 is used for degassing
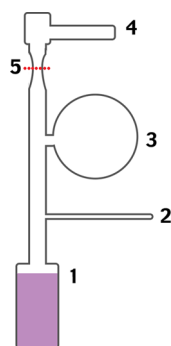

Figure 1. Reaction vessel.

(freeze−pump−thaw degassing of liquid), when the solution is situated in compartment 3. For this, the solution, cooled with liquid nitrogen, was evacuated with a diffusion pump (2×10^{-3} mm Hg) and heated to room temperature. This cycle was repeated 5−6 times, then the ampule was sealed off along line 5. The quartz cuvette 1 ($l = 1$ cm) was used for the irradiation and registration of UV−vis absorption spectra. In such a realization of the experiment, there was a possibility of parallel recording of changes in the UV and ESR spectra during the reaction. In those cases, when only the UV or ESR spectra were being registered, a simplified variant of the vessel was used in which the UV cuvette or the ESR ampule was absent.

After degassing, the samples were exposed to the light of a high-pressure mercury lamp (500 W), equipped with a quartz focusing system, a water filter for the absorption of infrared radiation, and glass color filters for the selection of light with the necessary wavelength. The greater part of the experiments was performed using radiation with $\lambda > 390$ nm.

MALDI Mass Spectrometry. MALDI mass spectra were acquired using a Bruker AutoFlex II reflector time-of-flight mass spectrometer equipped with N_2 laser (337 nm, 2.5 ns pulse). The control system permitted recording post source decay (PSD) mass spectra. *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, ≥98%, Sigma-Aldrich) was chosen as a matrix, the matrix-to-analyte molar ratio in spotted probes being above 1000/1. This matrix of electron-exchanging type has been successfully used in MALDI studies of an enormous number of fullerene derivatives,[15] including $C_{60}(R_F)_{2k+1}^{\bullet}$ free radicals ($R_F = CF_3$, C_2F_5).[14,15]

High-Resolution ESI Mass Spectrometry. ESI high-resolution mass spectra (HRMS) were recorded using an AB Sciex TripleTOF 5600+ quadrupole-time-of-flight mass spec-

trometer equipped with DuoSpray ion source. The native samples were diluted with a toluene−methanol (1:1) mixture with the addition of CsI and directly injected in the ion source.

NMR Spectroscopy. NMR spectra of the synthesized compounds (1,2-diclorobenzene-d_4 solutions, 298 K) were recorded on a Bruker Avance III spectrometer at 600.13, 376.45, and 150.90 MHz for ^1H, ^{19}F, and ^{13}C, respectively.

ESR Spectroscopy. X-band ESR spectrometers Varian-E3 and Bruker-EMX-plus were used. The spectra were recorded in the temperature range 293−460 K for the samples after light irradiation or in situ directly under irradiation. To interpret the ESR spectra, a quantum chemical calculation of the spin density and hyperfine interaction (hfi) constants were performed at the density functional theory (DFT) level with the use of the PRIRODA package,[18] employing the original TZ2P basis set and a PBE exchange−correlation functional. This calculation technique was applied also for optimizing the geometry of identified radicals.

Liquid Chromatography. HPLC separations of reaction mixtures were performed using Waters chromatograph (a double-wave detector of absorption at 290 and 330 nm), equipped with Cosmosil Buckyprep column (10 mm × 250 mm), toluene was used as an eluent (4.6 mL/min). Analytical chromatograms were obtained using an Agilent 1100 series chromatograph equipped with an UV−vis diode array detector (190−950 nm) and Cosmosil Buckyprep column (4.6 mm × 250 mm). Toluene was used as an eluent (1 mL/min).

UV−Vis Spectroscopy. The absorption spectra were recorded in a quartz cuvette ($l = 1$ cm) on the spectrophotometer Shimadzu UV-2400PC. The UV−vis spectra for the initial reagents were in good agreement with published data.[19−21] The absorption bands of fullerene 404 and 408 nm were used for recording the reaction kinetic curve. For this purpose, the optical density at the wavelength 404 nm at different times of irradiation was measured relative to the baseline (Figure 2).

Counter-Synthesis. Synthesis of single bound fullerene dimer $(C_{60}C_4F_8I)_2$ was carried out using the procedure described in ref 22 with modifications according to the following scheme:
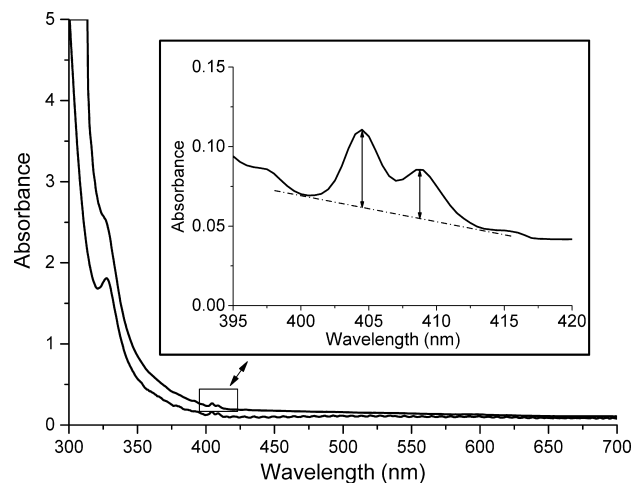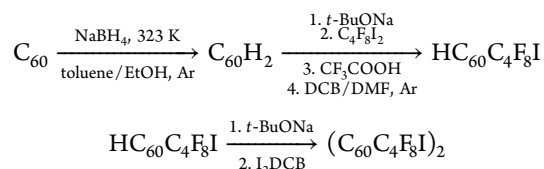

Figure 2. Optical spectra of the joint C_{60} and CF_3I solution (black), the sum of C_{60} and CF_3I spectra (gray). The inset presents determination of optical density (*A*) of the solution. The arrows show the measured values.

$$C_{60} \xrightarrow[\text{toluene/EtOH, Ar}]{\text{NaBH}_4,\ 323\ K} C_{60}H_2 \xrightarrow[\substack{3.\ CF_3COOH \\ 4.\ DCB/DMF,\ Ar}]{\substack{1.\ t\text{-BuONa} \\ 2.\ C_4F_8I_2}} HC_{60}C_4F_8I$$

$$HC_{60}C_4F_8I \xrightarrow[\text{2. I}_2DCB]{1.\ t\text{-BuONa}} (C_{60}C_4F_8I)_2$$

Synthesis of $C_{60}(C_4F_8I)H$. NaBH$_4$ (2 mg) solution in ethanol (4 mL) was added to the stirred solution of fullerene (100 mg) in toluene (100 mL) at 313−323 K by 1 mL portions with 10 min interval. The progress of the reaction was monitored by HPLC. After the reaction, the solution was passed through a silica column and dried *in vacuo*. The crude $C_{60}H_2$ was dissolved in *o*-dichlorobenzene under argon. Freshly prepared *t*-BuONa (25 mg) and 130 μL of $C_4F_8I_2$ were then added. On completion of the reaction, monitored by HPLC, an excess of trifluoroacetic acid was added. The obtained compound was chromatographically purified and characterized by NMR (S1) and ESI-HRMS (S2, Figure S2.1).

Synthesis of $(C_{60}(C_4F_8I))_2$. Freshly prepared *t*-BuONa (15 mg) was added to the solution of $C_{60}(C_4F_8I)H$ in *o*-dichlorobenzene/dimethylformamide (5:1). The solution became green. Then an iodine (30 mg) solution in *o*-dichlorobenzene was added. The progress of the reaction was monitored by HPLC. The product was purified by semi-preparative HPLC and characterized by ESI-HRMS (S2, Figure S2.2).

■ RESULTS

Photochemical Synthesis. We have examined the possibility of producing $C_{60}(C_4F_8)_n$ in the course of a heterogeneous reaction of fullerene C_{60} with $C_4F_8I_2$ under UV irradiation. By analogy with the method described in ref 23, an excess of $C_4F_8I_2$ was added to a suspension of fullerene in hexafluorobenzene and the mixture was then irradiated with the full light of a mercury lamp over 24 h. The MALDI mass spectrum showed the peak of initial fullerene only. Thus, the reaction did not proceed in these conditions.

A homogeneous reaction in the solution of C_{60} and $C_4F_8I_2$ under UV radiation was also tested. A 20 mg sample of C_{60}, 1,2-dichlorobenzene as a solvent, and an excess of $C_4F_8I_2$ were placed in a quartz ampule, which subsequently was pumped, sealed, and subjected to mercury lamp UV radiation over 1−14 h without using light filters. Full conversion of the fullerene was observed within 5.5 h. The reaction forms compounds of the following composition: $C_{60}(C_4F_8I)_n$ (n = 1−5), $C_{60}(C_4F_8I)_n(C_4F_8)_m$ (n = 1, 3, 5; m = 1, 2). Compounds of the composition $C_{60}(C_4F_8I)_nCl_x$ were detected by MALDI mass spectra along with −C_4F_8− derivatives of C_{60}. Chlorine-containing derivatives complicate considerably the obtained mixture of products and subsequent chromatographic separation. These results show the possibility of photochemical reactions under UV radiation. However, a wide variety of products including chlorine-containing products was formed. Obviously, dichlorobenzene was a participant of the reaction as well. For the purpose of more detailed investigation we carried out the photochemical synthesis in softer and more controlled conditions.

Photochemical Reaction of C_{60} with CF_3I. In a preliminary experiment it was found that CF_3I is highly soluble in hexane, so the concentration of CF_3I can be 10^3 times higher than the concentration of fullerene. Optical absorption spectra

of the mixed solutions of C_{60} and CF_3I in hexane are shown in Figure 2.

The sum of the spectra of the individual solutions C_{60} in hexane and CF_3I in hexane with the same concentrations is presented in Figure 2 for comparison. One can see that these two spectra do not coincide. The shape of the absorption bands of fullerene in mixed solution (see, for example the peak at 329 nm) differs from the same bands in the individual solution. In addition, an increase of absorption in the wavelength range λ < 600 nm is observed. These results show that the spectra are not additive and thus prove a considerable formation of a complex between fullerene and CF_3I. It seems most probable that the formation of the complexes is caused by charge transfer between the reagents. Similar results were obtained for all perfluorinated iodides investigated. The charge transfer complexes of fullerene with polynuclear aromatic hydrocarbons and substituted anilines were observed earlier.[24−27]

The irradiation of the solution with light of different wavelengths was performed to elucidate the photochemically active compounds. Photochemical reaction was found to proceed rapidly under irradiation with light in the visible range λ > 390 nm. The changes in the absorption spectra of C_{60}/CF_3I solution in hexane in the course of the irradiation are shown in Figure 3.

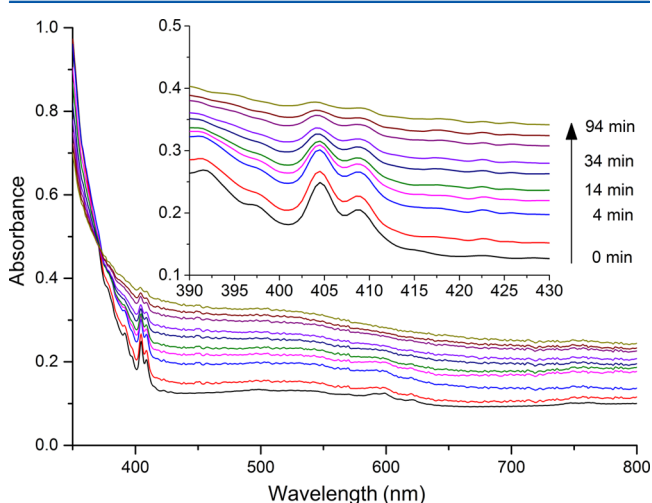**Figure 3.** UV−vis absorption spectra of C_{60}/CF_3I in decalin at different irradiation times, λ > 390 nm.

One can see in Figure 3 that the intensities of the absorption bands of C_{60} at 404 and 408 nm decrease in the course of irradiation by light. The change in the optical density allows determining the kinetics of the consumption of the initial fullerene. The kinetic data will be discussed below. An increase in the extinction in the wide wavelength range >400 nm is observed as well. Most likely, this extinction is the result of light scattered by low-solubility products of the reaction. Typical MALDI mass spectra for the samples after irradiation are present in Figure 4. The singly substituted product $C_{60}CF_3$ and the initial fullerene dominate. The products with two CF_3 groups are present in much smaller amounts, whereas highly substituted compounds are almost absent. A small amount of the product, corresponding to $C_{60}CF_3O$, is likely the result of reaction with oxygen during preparation of the probe for mass spectroscopy.
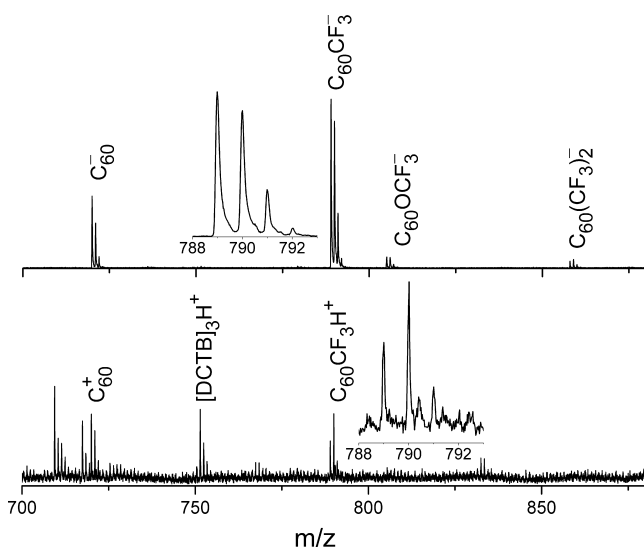
Figure 4. Negative (top) and positive (bottom) MALDI spectra of a sample after irradiation ($\lambda > 390$ nm) of C_{60} and CF_3I in hexane. Insets: mass spectra scaled in the mass range 788.5−793.0.

ESR spectroscopy shows the absence of paramagnetic particles at room temperature. However, a weak signal appears as the temperature increases. The observed ESR spectrum (Figure 5) consists of four lines, corresponding to the hyperfine
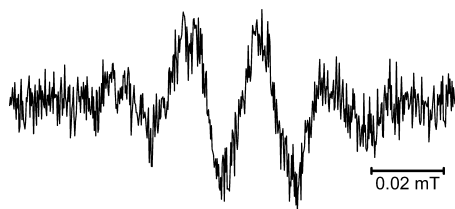

Figure 5. ESR spectrum of a C_{60}/CF_3I solution in decalin after irradiation ($\lambda > 390$ nm) over 60 min (423 K).

interaction of the unpaired electron with three fluorine nuclei. The characteristics of this spectrum will be discussed below.

The results indicate that photochemical reaction of trifluoromethylation between C_{60} and CF_3I is induced effectively by visible light. Light absorption by CF_3I molecules is virtually absent in the used wavelength range. Therefore, the observed photochemical transformation of the initial substances is caused by excitation in the absorption band of the fullerene or by the charge transfer band of the complex $C_{60} \cdot CF_3I$.

Photochemical Reaction of C_{60} with $C_2F_4I_2$. Irradiation of $C_{60}/C_2F_4I_2$ hexane solutions in similar conditions (room temperature, $\lambda > 390$ nm) demonstrates results similar to the C_{60}/CF_3I system. The decrease of the C_{60} absorption band and the formation of the product of single C_2F_4I-group addition to the fullerene sphere are observed. The optical absorption and the MALDI spectra are shown in S3 (Figure S3.1) and S2 (Figure S2.3). However, the progress of the photochemical reaction in the $C_{60}/C_2F_4I_2$ system was considerably slower in comparison with the C_{60}/CF_3I system. After irradiation for 280 min, only 21% conversion of the initial fullerene was achieved in *o*-dichlorobenzene solution. One specific feature of $C_{60}/C_2F_4I_2$ solutions is the presence of elemental iodine among the reaction products. Iodine is clearly registered in the spectra as a

characteristic absorption band with a maximum at 499 nm in toluene and 504 nm in *o*-dichlorobenzene (S3, Figure S3.2).

The above-mentioned peculiarities are obviously connected with the low stability of the radical $C_2F_4I^\bullet$. It is known[13] that the $C_2F_4I^\bullet$ radical eliminates the iodine atom with a characteristic time of 25 ps to form the stable molecule $F_2C=CF_2$. This process competes with the bimolecular reaction of $C_2F_4I^\bullet$ radical attachment to fullerene and decreases the yield of the products of addition. The iodine atoms, formed in the course of dissociation of $C_2F_4I^\bullet$ radical, recombine to form molecular iodine. The described features point to the radical mechanism of photochemical reaction in $C_{60}/C_2F_4I_2$ system.

Photochemical Reaction of C_{60} with $C_4F_8I_2$. The changes in the optical absorption spectra of a solution of $C_{60}/C_4F_8I_2$ in hexane under irradiation with $\lambda > 390$ nm are similar to those described above for the C_{60}/CF_3I system (S3, Figure S3.3). Similar spectral changes were observed when toluene, trichlorobenzene, or benzene was used as the solvent. Measurements of the fullerene absorption in the 404 nm band revealed that conversion of fullerene is sensitive to the reagent concentration. MALDI mass spectra of the reaction products pointed to the presence of species containing from 1 to 4 C_4F_8I-groups, $C_{60}C_4F_8I^\pm$ peaks being dominant (S2, Figure S2.4). The MALDI spectra are discussed in detail in S4.

The solutions $C_{60}/C_4F_8I_2$ directly under irradiation demonstrated an ESR signal (S7, Figure S7.1) that vanished in the dark at room temperature. The same ESR spectrum was observed when the solution after irradiation was heated (S7, Figure S7.2). In our experiments, the strong temperature dependence of the spectrum was reversible up to 400 K. Along with the increase of the signal intensity with temperature, improvement of the spectral resolution was observed. The most resolved ESR spectrum is presented in Figure 6.
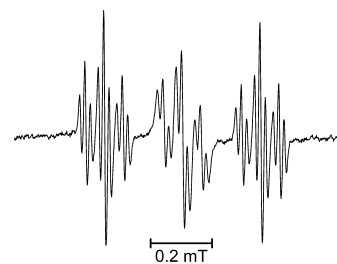

Figure 6. ESR spectrum of the fraction p6 at 453 K.

It corresponds to the hyperfine structure resulting from the interaction of the unpaired electron with three different pairs of fluorine atoms. A more detailed analysis of this spectrum is given below. We notice here only that the ESR spectrum belongs to a radical particle $C_{60}C_4F_8I^\bullet$.

The observed temperature dependence of ESR spectrum is similar to that described in the literature for other radical fullerene intermediates.[16,28] It has been shown to be the result of the reversible formation of dimers with a weak fullerene–fullerene σ-bond. Thus, the observed temperature dependence of the ESR spectra points to a reversible equilibrium in the reaction $2C_{60}C_4F_8I^\bullet \leftrightarrows (C_{60}C_4F_8I)_2$.

The products of the photochemical reaction of C_{60} with $C_4F_8I_2$ were subjected to chromatographic separation using toluene as an eluent. The chromatogram of the reaction mixture is presented in Figure 7. The peak marked p0
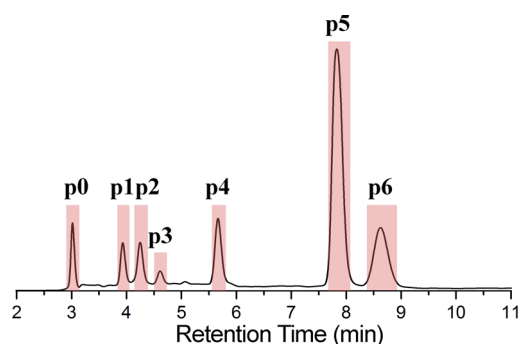
Figure 7. Chromatogram of the products of irradiation of the C_{60}/$C_4F_8I_2$ mixture in toluene.

corresponds to the solvent of the reaction mixture. Six fractions, marked in Figure 7 as p1–p6, were obtained from the reaction mixture using preparative chromatography.

The main peaks in the positive and negative MALDI mass spectra of the fractions p1–p3 and p6 were $C_{60}C_4F_8I^\pm$; their isotopic abundances correspond to that calculated for $C_{60}C_4F_8I$. For the fraction p5 the main signals referred to the initial fullerene. The fraction p4 was indicated by MALDI mass spectra (S2, Figure S2.5, S4) to be mainly constituted by the hydrogenated derivative $C_{60}(C_4F_8I)H$. The ESR spectra of all the fractions showed an identical shape of the signal. However, the concentration of paramagnetic particles for p6 was an order of magnitude higher than for the other fractions. Thus, paramagnetic particles in all cases except for the p6 fraction were, presumably, an insignificant admixture.

To elucidate the thermal stability of the constituents of p1–p6, they were annealed for 1–3 h and subsequently analyzed by HPLC and MALDI mass spectrometry. It was established that the composition of p4 and p5 had not changed after heating, whereas for p1–p3 and p6 the composition underwent changes (Table 1). Rows in Table 1 show the composition of the

Table 1. Composition of the Chromatographic Fractions after Heating

original fraction (T_{an}, K)[a]	p4, % $C_{60}(C_4F_8I)H$ 5.7 min	p5, % C_{60} 8.0 min	p6, % $(C_{60}C_4F_8I)_2$ 8.8 min	retention time (min) and relative content (%) of minor products
p1 (423)	27	28	28	3.6 (4%); 4.1 (2%); 5.1 (6%); 6.2 (5%)
p2 (423)	22	39	12	3.5 (3%); 4.1 (5%); 4.7 (3%); 5.1 (11%); 6.2 (5%)
p3 (423)	26	31	18	3.6 (1%); 4.7 (8%); 5.1 (14%); 6.2 (2%)
p6 (453)	10	74	4	4.2 (1%); 5.1 (10%); 6.2 (1%)

[a]Annealing temperature, K.

chromatographic fractions after heating of the fraction indicated in the first column. The second row, for example, demonstrates that heating of the fraction p1 leads to formation of the compounds, which are identical to the fractions p4, p5, and p6 of the reaction mixture. The additional chromatographic peaks for solution p1 after heating are listed in the last column.

It is seen on the whole that heating of every fraction produces the same main products, compounds p4–p6. The relative contents of these products is presented in columns 2–4

of the table. The retention times and the relative contents (in brackets) of the chromatographic peaks for most distinct minor products are presented in the last column.

Counter-Synthesis of $C_{60}C_4F_8IH$ and the Dimer ($C_{60}C_4F_8I)_2$. The assumed dominant product of the studied photochemical reaction ($C_{60}C_4F_8I)_2$ was not observed in the MALDI spectra. That was the cause for the counter-synthesis of this compound undertaken in the present work. The product $C_{60}C_4F_8IH$, obtained at the first stage of the synthesis, was extracted individually and characterized with MALDI and highly resolved ESI mass spectra as well as with ^1H, ^{19}F, and ^{13}C NMR (S2, Figure S2.1 and S1). The obtained compound was found to be the mixture of two isomers with *ortho* and *para* positions of the H atom relative to the C_4F_8I group in a 3:1 ratio. Comparing the analytical chromatograms and the light absorption spectra of the synthesized hydrogenated product $C_{60}C_4F_8IH$ (S3, Figure S3.4, S5, Figure S5.1) with those for the fraction p4 (S3, Figure S3.5, S5, Figure S5.2), one can see that these compounds are identical in the retention times and spectral details. Hence, the fraction p4 was identified as *o*-$C_{60}C_4F_8IH$.

The synthesized dimer ($C_{60}C_4F_8I)_2$ was characterized by HPLC, MALDI and ESI mass spectrometry, and ESR spectra. In ESI mass spectrum of the counter-synthesis products $[(C_{60}C_4F_8I)_2 + I]^-$ peak was present. The HPLC trace, MALDI mass spectra, and ESR spectra for the dimer appeared to be identical to those for the p6 fraction of the product of irradiation.

■ DISCUSSION

The results described above show that fullerene molecules are able to form complexes with perfluorinated iodides in solution. These complexes are seen as the extra absorption in the UV–vis spectra. Irradiation with light in the range $\lambda > 390$ nm is absorbed in the band of the complex and in the band of fullerene as well. The ESR spectra observed in the course of photochemical transformation indicate the free-radical mechanism of the reaction. It is known that a population of low-lying exited states of fullerene occurs in the course of irradiation.[29] The energy of these states, as well as the photon energy, is not high enough, however, to populate the excited states of alkyl iodides. It should be concluded that the observed photochemical reaction cannot be the result of the homolytic photodissociation of the C–I bond but is the result of photoinduced electron transfer. The absorption of light in the charge transfer band of observed complex seems to be more favorable for this reaction. Photochemical functionalization of fullerene through the electron transfer mechanism is described in the literature. Photoaddition of amines are the most studied reaction of this type.[30,31] This reaction includes electron transfer from the amine to the fullerene cage. It means that the fullerene is the electron acceptor component of the reactions. It is known that a photoredox catalyst can be used for a more effective generation of aminoalkyl radicals in this reaction.[32] The photoinduced electron transfer in the opposite direction with generation of fullerene cation-radicals was described in the presence of 9,10-dicyanoanthracene with biphenyl as a charge carrier.[33] Dissociative electron transfer is known to be a peculiar feature of the organic alkyl iodides.[34−37] Thus, photoinduced dissociative electron transfer from excited fullerene to perfluorinatedalkyl iodides seems to be responsible for the generation of radicals in the considered reaction.

Measuring the optical density in the fullerene absorption band gives the kinetics of the fullerene consumption in the course of the photochemical reaction. The obtained kinetic curve in the case $C_{60}/C_4F_8I_2$ system is depicted in Figure 8. One can see that the kinetics correspond to a second-order reaction. The kinetic curves of the reaction in the C_{60}/CF_3I system are presented in S6 (Figure S6.8).
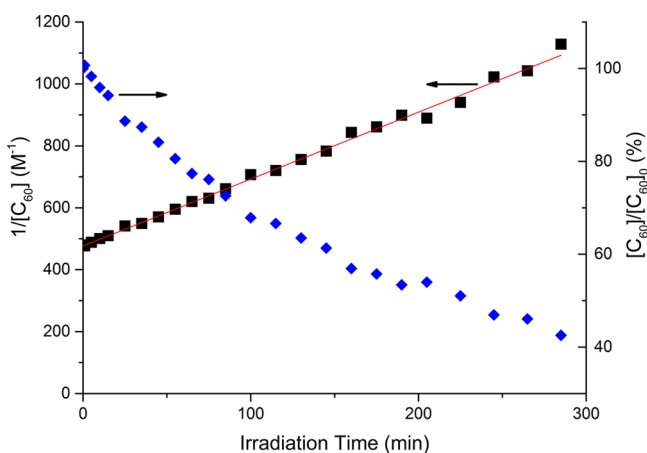

Figure 9. Geometry of the active intermediate in photochemical reaction of C_{60} with $C_4F_8I_2$. Positions 2 and 4 on the fullerene cage are marked by numbers.

Figure 8. Kinetic curves for the consumption of fullerene in the reaction with $C_4F_8I_2$.

The post irradiation ESR spectrum of C_{60}/CF_3I solution in decalin, recorded at 423 K, is presented in Figure 4. The signal is a quadruplet with the ratio 1:3:3:1 and the hfi constant a_F = 0.02 mT. The spectrum for $C_{60}CF_3$ at 425 K in a toluene solution is described in the literature.[38] It is also a quadruplet with a_F = 0.018 mT. It is shown in the cited work that at low temperatures one can observe six peaks with relative intensities 1:2:1:1:2:1, which refer to the splitting on the two equivalent nuclei ^{19}F with $a_F(2)$ = 0.028 mT and single ^{19}F with $a_F(1)$ = 0.063 mT. The shape of the ESR spectrum is known to be temperature dependent. The changes in the signal shape with temperature are connected with hindered rotation of the $-CF_3$ group at low temperatures, whereas faster rotation at higher temperatures make the three fluorine atoms equivalent. We failed to record the low-temperature ESR spectra because of low signal intensities. Our value a_F = 0.02 mT (423 K) in decalin is close to that in literature (0.018 mT, toluene, 425 K).

As already noted above, the ESR spectrum for the products of the photochemical reaction in the $C_{60}/C_4F_8I_2$ system shows the strong temperature dependence as well. The most resolved spectrum (453 K, Figure 6) corresponds to a hyperfine splitting on the three pairs of fluorine atoms (a_1 = 0.254, a_2 = 0.060, a_3 = 0.018 mT) and should be interpreted as splitting on the fluorine atom pairs $-CF_2-$ in $-C_4F_8I$ substitute. Every subsequent difluoromethylene group is situated farther from the fullerene cage and therefore demonstrates a lower hyperfine constant (Figure 9).

DFT calculations of the molecular geometry and hfi constants for $C_{60}C_4F_8I^{\bullet}$ were performed for verification of this interpretation of the ESR spectrum. Because free rotation around the $C_{60}-C_4F_8I$ bond is possible at high temperatures, the geometry of $C_{60}C_4F_8I^{\bullet}$ was optimized step-by-step (30°) for the torsion angles 0−360° between the C_4F_8I group and the fullerene sphere. The values of the constants were averaged over a Boltzmann distribution using the energies of the obtained geometries of rotamers. The values of the hyperfine
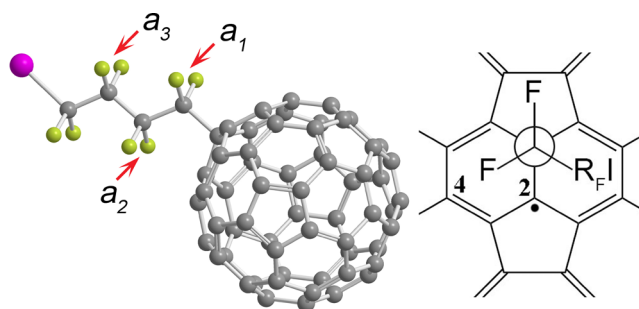
constants was calculated to be a_1 = 0.26, a_2 = 0.04, a_3 = 0.006 mT at 463 K. These values are in satisfactory agreement with our experimental ESR observations. Thus, we conclude that the observed ESR spectrum belongs to a free-radical adduct $C_{60}C_4F_8I^{\bullet}$ with the geometry shown in Figure 9.

The hindered rotation of the substitute causes the broadening of the ESR spectrum and changes the intensity ratios of the spectral components. Similar changes with temperature for other radicals are known in the literature and are called the alternation of spectral lines.[39]

The temperature dependence of the concentration of paramagnetic particles in the solution can be obtained by numerical double integration of the spectra. The spectra at higher modulation amplitude (S7, Figure S7.2) were recorded for more accuracy of the integration procedure. The obtained temperature dependencies of the total number of paramagnetic particles reflect equilibrium in the reaction $2C_{60}C_4F_8I^{\bullet} \leftrightarrows (C_{60}C_4F_8I)_2$ (S7, Figure S7.3). Using the temperature dependence, it is easy to estimate (S7.2−S7.7) the value of dimerization enthalpy, which comprises 103.3 ± 10.5 kJ/mol. Probably, such a low value of the bond energy for the dimer results from the steric hindrance induced by the $-C_4F_8I$ groups.

Chromatographic results for the products of the photochemical transformations in $C_{60}/C_4F_8I_2$ system clarify the structure of the reaction products. It is known that substituted derivatives of fullerenes have less retention time than the original fullerene.[11,40] In the case under consideration, such substituted fullerenes are represented by fractions p1−p4. The light absorption spectra can be used to determine the location of substitutes on the fullerene sphere. In particular, the counter-synthesis proves that p4 is the monohydrated fullerene $C_{60}C_4F_8IH$. The UV−vis spectrum of this compound (S3, Figure S3.5) has a narrow absorption band at 432 nm, which points to 1,2-addition of the substitutes.[41−45] Thus, the hydrogen atom is found in *ortho*-position to C_4F_8I. The fraction p6 consists of the dimer $(C_{60}C_4F_8I)_2$, which has a longer retention time than fullerene itself. The UV−vis spectrum of p6 has a wide absorption band at 448 nm (S3, Figure S3.6). It is known that such an absorption band with a maximum around 450 nm is characteristic of 1,4-substituted fullerenes.[46−49] Thus, fraction p6 is a 1,4,1′,4′-dimer $(C_{60}C_4F_8I)_2$, both parts of which are para-substituted. This conclusion is in agreement with available data in the literature.[17,22]
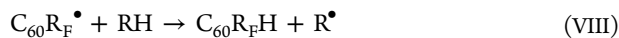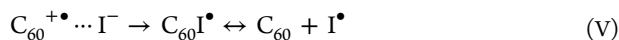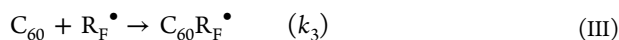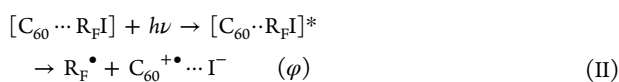
Fractions p1 and p2 also show bands with a maximum about 450 nm (S3, Figures S3.7, S3.8) in the UV−vis spectra and thus can be attributed to 1,4-bisubstituted fullerenes. No additional bands are observed in the absorption spectra of the p3 fraction

(S3, Figure S3.9). So, we have no data concerning the structure of this compound.

The chromatographic analysis of the fractions p1−p3 and p6 after heating (S5, Figure S5.3−5.6) shows that these compounds have relatively low stability (Table 1). The composition of the products after thermal decomposition is approximately identical. Presumably, it is governed by the reactions of the radical monoadduct $C_{60}C_4F_8I^•$, which is the primary product of thermal decomposition in all cases. It is likely that p1−p3 are bisubstituted compounds $XC_{60}C_4F_8I$ with labile $X−C_{60}$ bond. One can suppose that among them are compounds of composition $IC_{60}(C_4F_8I)$ with the iodine atom on the fullerene cage in different isomer positions. Substances with iodine attached to the fullerene cage have not been studied because the low stability of the fullerene−carbon−iodine bond. The sole compound characterized up to now is the iodinated fullerene stabilized by four adjacent peroxy-*tert*-butyl substitutes.[50] The formation of fullerene derivatives, containing an IO substitute and other derivatives with polyvalent iodine, is also not excluded.[51−55]

The results, presented in Table 1, show that compounds p1−p3 are able to decompose to initial fullerene. Besides that, the products of trans alkylation with formation of polysubstituted derivatives $C_{60}(C_4F_8I)_n$ appear. Such reactions at heating are known for other perfluoroalkyl derivatives of fullerene. For example, annealing a sample of a mixture of C_{60} and $C_{60}(CF_3)_{12}$ at the temperature 803 K for 20 min leads to the generation of the compound $C_{60}(CF_3)_6$.[55]

Summarizing the experimental results, one can offer the following scheme of photochemical reactions:

$$C_{60} + R_FI \leftrightarrow [C_{60}\cdots R_FI] \qquad (K_{eq}) \qquad (I)$$

$$[C_{60}\cdots R_FI] + h\nu \rightarrow [C_{60}\cdots R_FI]^*$$
$$\rightarrow R_F^• + C_{60}^{+•}\cdots I^- \qquad (\varphi) \qquad (II)$$

$$C_{60} + R_F^• \rightarrow C_{60}R_F^• \qquad (k_3) \qquad (III)$$

$$R−H + R_F^• \rightarrow R_FH + R^• \qquad (k_4) \qquad (IV)$$

$$C_{60}^{+•}\cdots I^- \rightarrow C_{60}I^• \leftrightarrow C_{60} + I^• \qquad (V)$$

$$2C_{60}R_F^• \leftrightarrow (C_{60}R_F)_2 \qquad (VI)$$

$$C_{60}R_F^• + I^• \leftrightarrow IC_{60}R_F \qquad (VII)$$

$$C_{60}R_F^• + RH \rightarrow C_{60}R_FH + R^• \qquad (VIII)$$

Reaction I in this scheme describes the equilibrium formation of the complex of fullerene with iodide. Reaction II presents the primary photochemical reaction of this complex. It is the photoinduced electron transfer, followed by cleavage of the iodide ion and the formation of a perfluorinated radical. Reaction III is the formation of the radical adduct, which is the main reaction intermediate. Reaction IV indicates the competing interaction of perfluorinated radical with solvent molecules. Reactions V−VII reflect further transformations of radical and ionic intermediates. In accordance with this scheme, the concentration of the fullerene varies only in reaction III. Only those processes that lead to products registered in our experiments are reflected in the scheme. The scheme explains the presence of the hydrogenated derivative $C_{60}R_FH$, the fullerene derivative with iodine on the sphere $IC_{60}R_F$, as well as

the lack of molecular iodine, atoms of which recombine with the radicals $R^•$ and $C_{60}R_F^•$.

Reactions I, II, and V describe essentially the action of the fullerene as a photocatalyst, which works by mechanism of reversible electron transfer. The photocatalitic activity of the heterogeneous carbon materials was reported earlier.[56,57]

Detailed kinetic analysis of the first four reactions of the proposed scheme is given in S6. It leads to the following results. The photochemical reaction rate is described by the equation

$$\frac{d[C_{60}]_\Sigma}{dt} = -k_{eff}[C_{60}]_\Sigma^2$$

$$k_{eff} = \frac{k_3 I_0 \varepsilon l \varphi K_{eq}}{k_4[RH](K_{eq}[R_fI] + 1)^2} \qquad (1)$$

where I_0 is the intensity of the incident light, ε is the optical absorption coefficient of the complex, l is length of the optical path, and φ is the quantum yield of the primary photochemical reaction.

Equation 1 is a kinetic equation of the second-order relative to the concentration of fullerene. Equation 1 after integration presents a straight line in the coordinates $1/[C_{60}]$ *vs* t:

$$\frac{1}{[C_{60}]_\Sigma} = k_{eff}t + \frac{1}{[C_{60}]_0} \qquad (2)$$

The experimental results, shown in Figure 8 and S6.8, are in good agreement with eq 2. The values of the effective rate constants for the reaction of C_{60} with CF_3I, calculated from the experimental data, were k_{eff} = 884 $M^{-1}\cdot min^{-1}$ in *n*-hexane and 1.72 $M^{-1}\cdot min^{-1}$ in *trans*-decalin. The effective rate constant for the reaction of C_{60} with $C_4F_8I_2$ was k_{eff} = 3.65 $M^{-1}\cdot min^{-1}$ in benzene solution and k_{eff} = 2.1 $M^{-1}\cdot min^{-1}$ in toluene. The values correlate with the energy of the R−H bond in the molecules of the solvent. Indeed, the weaker this bond, the greater is the rate constant k_4 competing with reactions IV and, in full accordance with the expression 1, the lower is the value of the effective rate constant of the fullerene consumption.

CONCLUSION

The photochemical reaction of fullerene and perfluoroalkyl iodides under irradiation by visible light is initiated by the excitation of the fullerene component and the dissociative electron transfer to iodide with generation of radical species. The photocatalitic character of the reaction is proved by the bimolecular kinetic law of the reaction. The most important intermediate is the product of the attachment of the radical to a fullerene molecule ($C_{60}R_F^•$). Symmetrical recombination of this intermediate leads to the formation of a single bound dimer. The second iodine atom of diiodide, however, is not activated photochemically and can be used for further synthetic modifications such as attachment of a donor moiety to create perfluoroalkylene-linked photovoltaic dyads. The dimer product of the reaction is moderately stable at room tempetarure. It is able to undergo further transformations and provide an approach toward controlled functionalization of various materials.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.6b10718.

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The authors declare no competing financial interest.

■ REFERENCES

(1) Hirsch, A.; Brettreich, M. *Fullerenes: Chemistry and Reactions*; Wiley-VCH: Weinheim, 2005.

(2) Fagan, P. J.; Krusic, P. J.; McEwen, C. N.; Lazar, J.; Parker, D. H.; Herron, N.; Wassermann, E. Production of Perfluoroalkylated Nanospheres from Buckminsterfullerene. *Science* **1993**, *262*, 404−407.

(3) Morton, J. R.; Negri, F.; Preston, A. F. Addition of Free Radicals to C_{60}. *Acc. Chem. Res.* **1998**, *31*, 63−69.

(4) Popov, A. A.; Kareev, I. E.; Shustova, N. B.; Stukalin, E. B.; Lebedkin, S. F.; Seppelt, K.; Strauss, S. H.; Boltalina, O. V.; Dunsch, L. Electrochemical, Spectroscopic, and DFT Study of $C_{60}(CF_3)_n$ Frontier Orbitals ($n = 2$−18): The Link between Double Bonds in Pentagons and Reduction Potentials. *J. Am. Chem. Soc.* **2007**, *129*, 11551−11568.

(5) Ignat'eva, D. V.; Mutig, T.; Goryunkov, A. A.; Tamm, N. B.; Kemnitz, E.; Troyanov, S. I.; Sidorov, L. N. New $C_{70}(CF_3)_n$ isomers (n = 12, 14, 16). Realkylation and Addend Rearrangements. *Russ. Chem. Bull.* **2009**, *58*, 1146−1154.

(6) Tamm, N. B.; Avdoshenko, S. M.; Kemnitz, E.; Troyanov, S. I. Synthesis, Structural Investigation, and Theoretical Study of Pentafluoroethyl Derivatives of [60]Fullerene. *Russ. Chem. Bull.* **2007**, *56*, 915−921.

(7) Tamm, N. B.; Troyanov, S. I. Synthesis and Molecular Structure of Seven Isomers of $C_{70}(C_2F_5)_{10}$. *Mendeleev Commun.* **2007**, *17*, 172−174.

(8) Mutig, T.; Avdoshenko, S. M.; Kemnitz, E.; Troyanov, S. I. Synthesis and Molecular Structures of Heptafluoroisopropylated Fullerenes: $C_{60}(i$-$C_3F_7)_8$, $C_{60}(i$-$C_3F_7)_6$, and $C_{60}(CF_3)_2(i$-$C_3F_7)_2$. *J. Fluorine Chem.* **2009**, *130*, 241−247.

(9) Mutig, T.; Kemnitz, E.; Troyanov, S. I. Synthesis and Structural Characterization of Four Isomers of $C_{70}(n$-$C_3F_7)_8$. *Eur. J. Org. Chem.* **2008**, *2008*, 3256−3259.

(10) Pimenova, A. S.; Sidorov, L. N.; Kemnitz, E.; Troyanov, S. I. Fluorocycloalkylated Fullerenes in the Systems $C_{60/70}$−$C_2F_4I_2$. *Eur. J. Org. Chem.* **2007**, *2007*, 4999−5002.

(11) Gruzinskaya, N. I.; Pimenova, A. S.; Khavrel', P. A.; Sidorov, L. N.; Kemnitz, E.; Troyanov, S. I. Octafluorocyclohexa Derivatives of [60]Fullerene: $C_{60}(C_4F_8)_n$ (n = 2, 3, 4, and 6). *Russ. Chem. Bull.* **2009**, *58*, 2276−2282.

(12) Cao, J.; Ihee, H.; Zewail, A. H. Ultrafast Electron Diffraction and Direct Observation of Transient Structures in a Chemical Reaction. *Proc. Natl. Acad. Sci. U. S. A.* **1999**, *96*, 338−342.

(13) Zhong, D.; Ahmad, S.; Zewail, A. H. Femtosecond Elimination Reaction Dynamics. *J. Am. Chem. Soc.* **1997**, *119*, 5978−5979.

(14) Vorobiev, A. Kh.; Markov, V. Yu.; Samokhvalova, N. A.; Samokhvalov, P. S.; Troyanov, S. I.; Sidorov, L. N. Stable

(15) Markov, V. Yu.; Borschevsky, A. Ya.; Sidorov, L. N. MALDI Mass Spectrometry of Fullerene Derivatives. *Int. J. Mass Spectrom.* **2012**, *325*, 100−112.

(16) Morton, J. R.; Preston, K. F.; Krusic, P. J.; Wasserman, E. Electron Paramagnetic Resonance Spectra of R-C_{60} Radicals. Evidence for $RC_{60}C_{60}R$ Dimers. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1425−1429.

(17) Sabirov, D. Sh.; Garipova, R. R.; Bulgakov, R. G. Density Functional Theory Study on the Decay of Fullerenyl Radicals $RC_{60}^{\bullet}$, $ROC_{60}^{\bullet}$, and $ROOC_{60}^{\bullet}$ (R = tert -Butyl and Cumyl) and Polarizability of the Formed Fullerene Dimers. *J. Phys. Chem. A* **2013**, *117*, 13176−13183.

(18) Laikov, D. N. Fast Evaluation of Density Functional Exchange-Correlation Terms Using the Expansion of the Electron Density in Auxiliary Basis Sets. *Chem. Phys. Lett.* **1997**, *281*, 151−156.

(19) Leach, S.; Vervloet, M.; Despres, A.; Breheret, E.; Hare, J. P.; Dennis, T. J.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. Electronic Spectra and Transitions of the Fullerene C_{60}. *Chem. Phys.* **1992**, *160*, 451−466.

(20) Ajie, H.; Alvarez, M. M.; Anz, S. A.; Beck, R. D.; Diederich, F.; Fostiropoulos, K.; Huffman, D. R.; Kratschmer, W.; Rubin, Y.; Schriver, K. E.; Sensharma, D.; Whetten, R. L. Characterization of the Soluble All-carbon Molecules C_{60} and C_{70}. *J. Phys. Chem.* **1990**, *94*, 8630−8633.

(21) Haszeldine, R. N. Studies in Spectroscopy. Part III. The Ultra-violet Absorption Spectra of Halogen-Containing Aliphatic Iodo-Compounds, and the Relative Stability of Free Halogen-containing Alkyl Radicals. *J. Chem. Soc.* **1953**, 1764−1771.

(22) Cheng, F.; Murata, Y.; Komatsu, K. Synthesis, X-ray Structure, and Properties of the Singly Bonded C_{60} Dimer Having Diethoxyphosphorylmethyl Groups Utilizing the Chemistry of C_{60}^{2-}. *Org. Lett.* **2002**, *4*, 2541−2544.

(23) Shustova, N. B.; Kuvychko, I. V.; Peryshkov, D. V.; Whitaker, J. B.; Larson, B. W.; Chen, Yu.-S.; Dunsch, L.; Seppelt, K.; Popov, A. A.; Strauss, S. H.; et al. Chemical Tailoring of Fullerene Acceptors: Synthesis, Structures and Electrochemical Properties of Perfluoroisopropylfullerenes. *Chem. Commun.* **2011**, *47*, 875−877.

(24) Datta, K.; Banerjee, M.; Seal, B. K.; Mukherjee, A. K. Ground State EDA Complex Formation between [60]Fullerene and a Series of Polynuclear Aromatic Hydrocarbons. *J. Chem. Soc., Perkin Trans. 2* **2000**, *3*, 531−534.

(25) Sibley, S. P.; Campbell, J. R. L.; Silber, H. B. Solution and Solid State Interactions of C60 with Substituted Anilines. *J. Phys. Chem.* **1995**, *99*, 5274−5276.

(26) Bhattacharya, S.; Banerjee, M.; Mukherjee, A. K. Absorption Spectrometric Study of Molecular Complex Formation between [60]Fullerene and a Series of Methylated Pyridines. *Spectrochim. Acta, Part A* **2002**, *58*, 2563−2569.

(27) Bhattacharya, S.; Banerjee, M.; Mukherjee, A. K. Spectrophotometric and Thermodynamic Studies of [60]Fullerene/Methylbenzene Charge Transfer Complexes. *Spectrochim. Acta, Part A* **2003**, *59*, 3147−3158.

(28) Morton, J. R.; Preston, K. F.; Krusic, P. J.; Hill, S. A.; Wasserman, E. The Dimerization of Fullerene RC_{60} Radicals [R = alkyl]. *J. Am. Chem. Soc.* **1992**, *114*, 5454−5455.

(29) Ebbesen, T. W.; Tanigaki, K.; Kuroshima, S. Excited-State Properties of C_{60}. *Chem. Phys. Lett.* **1991**, *181*, 501−504.

(30) Nakamura, Y.; Suzuki, M.; O-kawa, K.; Konno, T.; Nishimura, J. Photoreactions between [60]Fullerene and Various Aromatic Tertiary Amines. *J. Org. Chem.* **2005**, *70*, 8472−8477.

(31) Lawson, G. E.; Kitaygorodskiy, A.; Sun, Y.-P. Photoinduced Electron-Transfer Reactions of [60]Fullerene with Triethylamine. *J. Org. Chem.* **1999**, *64*, 5913−5920.

(32) Miyake, Y.; Ashida, Y.; Nakajima, K.; Nishibayashi, Y. Visible-Light-Mediated Addition of α-Aminoalkyl Radicals to [60]Fullerene by Using Photoredox Catalysts. *Chem. - Eur. J.* **2014**, *20*, 6120−6125.

(33) Siedschlag, C.; Luftmann, H.; Wolff, C.; Mattay, J. Functionalization of [60]Fullerene by Photoinduced Electron Transfer

(PET): Syntheses of 1-substituted 1,2-dihydro[60]Fullerenes. *Tetrahedron* **1997**, *53*, 3587−3592.

(34) Bordwell, F. G.; Wilson, C. A. Distinguishing between Polar and Electron-Transfer Mechanisms for Reactions for Anions with Alkyl Halides. *J. Am. Chem. Soc.* **1987**, *109*, 5470−5474.

(35) Pause, L.; Robert, M.; Saveant, J.-M. Stepwise and Concerted Pathways in Photoinduced and Thermal Electron-Transfer/Bond-Breaking Reactions. Experimental Illustration of Similarities and Contrasts. *J. Am. Chem. Soc.* **2001**, *123*, 4886−4895.

(36) Gaillard, E. R.; Whitten, D. G. Photoinduced Electron Transfer Bond Fragmentations. *Acc. Chem. Res.* **1996**, *29*, 292−297.

(37) Cardinale, A.; Isse, A. A.; Gennaro, A.; Robert, M.; Saveant, J.-M. Dissociative Electron Transfer to Haloacetonitriles. An Example of the Dependency of In-Cage Ion-Radical Interactions upon the Leaving Group. *J. Am. Chem. Soc.* **2002**, *124*, 13533−13539.

(38) Morton, J. R.; Preston, K. F. Hindered Internal Rotation in Perfluoroalkyl-C_{60} Radicals. *J. Phys. Chem.* **1994**, *98*, 4993−4997.

(39) Wertz, J. E.; Bolton, J. R. *Electron spin resonance Elementary theory and Practical applications*; McGraw-Hill Book Company: New York, 1972.

(40) Dorozhkin, E. I.; Goryunkov, A. A.; Ioffe, I. N.; Avdoshenko, S. M.; Markov, V. Yu.; Tamm, N. B.; Ignat'eva, D. V.; Sidorov, L. N.; Troyanov, S. I. Synthesis, Structure, and Theoretical Study of Lower Trifluoromethyl Derivatives of [60]Fullerene. *Eur. J. Org. Chem.* **2007**, *2007*, 5082−5094.

(41) Mikami, K.; Matsumoto, S.; Ishida, A.; Takamuku, S.; Suenobu, T.; Fukuzumi, S. Addition of Ketene Silyl Acetals to the Triplet Excited State of C_{60} via Photoinduced Electron Transfer Leading to the Fullereneacetates. *J. Am. Chem. Soc.* **1995**, *117*, 11134−11141.

(42) Guldi, D. M.; Maggini, M.; Scorrano, G.; Prato, M. Intramolecular Electron Transfer in Fullerene/Ferrocene Based Donor−Bridge−Acceptor Dyads. *J. Am. Chem. Soc.* **1997**, *119*, 974−980.

(43) Fukuzumi, S.; Suneobu, T.; Kawamura, S.; Ishida, A.; Mikami, K. Selective Two-Electron Reduction of C_{60} by 10-methyl-9,10-dihydroacridine via Photoinduced Electron Transfer. *Chem. Commun.* **1997**, 291−292.

(44) Creegan, K. M.; Robbins, J. L.; Robbings, W. K.; Millar, J. M.; Sherwood, R. D.; Tindall, P. J.; Cox, D. M.; McCauley, J. P., Jr.; Jones, D. R. Synthesis and Characterization of $C_{60}O$, the First Fullerene Epoxide. *J. Am. Chem. Soc.* **1992**, *114*, 1103−1105.

(45) Smith, A. B., III; Strongin, R. M.; Brard, L.; Furst, G. T.; Romanow, W. J.; Owens, K. G.; King, R. C. 1,2-Methanobuckminsterfullerene (C61H2), the Parent Fullerene Cyclopropane: Synthesis and Structure. *J. Am. Chem. Soc.* **1993**, *115*, 5829−5830.

(46) Murata, Y.; Komatsu, K.; Wan, T. S. M. The Reaction of [60]Fullerene with Lithium Fluorenide: Formation of a Novel 1,4-adduct of [60]Fullerene. *Tetrahedron Lett.* **1996**, *37*, 7061−7064.

(47) González, R.; Wudl, F.; Pole, D. L.; Sharma, P. K.; Warkentin, J. An Unusual Addition−Rearrangement of a Dialkoxycarbene to C_{60}: Exclusion of Methanofullerene Products. *J. Org. Chem.* **1996**, *61*, 5837−5839.

(48) Subramanian, R.; Kadish, K. M.; Vijayashree, M. N.; Gao, X.; Jones, M. T.; Miller, M. D.; Krause, K. L.; Suenobu, T.; Fukuzumi, S. Chemical Generation of C_{60}^{2-} and Electron Transfer Mechanism for the Reactions with Alkyl Bromides. *J. Phys. Chem.* **1996**, *100*, 16327−16335.

(49) Fukuzumi, S.; Suenobu, T.; Hirasaka, T.; Arakawa, R.; Kadish, K. M. Formation of C_{60} Adducts with Two Different Alkyl Groups via Combination of Electron Transfer and S_N2 Reactions. *J. Am. Chem. Soc.* **1998**, *120*, 9220−9227.

(50) Huang, S.; Yang, X.; Zhang, X.; Hu, X.; Gan, L.; Zhang, S. Preparation of Covalent-Bound Iodofullerene through Selective Opening of Fullerene Epoxide To Form Halohydrin Fullerene Derivatives. *Synlett* **2006**, *2006*, 1266−1268.

(51) Merkushev, E. B. Organic Compounds of Polyvalent Iodine−Derivatives of Iodosobenzene. *Russ. Chem. Rev.* **1987**, *56*, 826−845.

(52) Maletina, I. I.; Orda, V. V.; Yagupol'skii, L. M. Fluorine-Containing Organic Derivatives of Polyvalent Halogens. *Russ. Chem. Rev.* **1989**, *58*, 544−558.

(53) Zhdankin, V. V.; Stang, P. J. Recent Developments in the Chemistry of Polyvalent Iodine Compounds. *Chem. Rev.* **2002**, *102*, 2523−2584.

(54) Zhdankin, V. V.; Stang, P. J. Chemistry of Polyvalent Iodine. *Chem. Rev.* **2008**, *108*, 5299−5358.

(55) Romanova, N. A.; Tamm, N. B.; Markov, V. Yu.; Goryunkov, A. A.; Sidorov, L. N.; Troyanov, S. I. Synthesis, X-ray Structure and Mass Spectrum of C_s-$C_{60}(CF_3)_6$. *Mendeleev Commun.* **2012**, *22*, 297−298.

(56) Zhang, N.; Yang, M.-Q.; Liu, S.; Sun, Y.; Xu, Y.-J. Waltzing with the Versatile Platform of Graphene to Synthesize Composite Photocatalysts. *Chem. Rev.* **2015**, *115*, 10307−10377.

(57) Han, C.; Zhang, N.; Xu, Y.-J. Structural Diversity of Graphene Materials and their Multifarious Roles in Heterogeneous Photocatalysis. *Nano Today* **2016**, *11*, 351−372.